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(54) Title: CATIONIC CLAYS AND USES IN PAPER AND PAINTS

(57) Abstract

Cationic kaolin clay which is useful as a filler and coating agent in paper and in paints, and as a pitch control agent in paper making processes, is produced by treating kaolin clay with 0.5 to 1.5 wt. % of aluminum chlorohydrate. The cationic clay, when added to an aqueous system containing paper fibers, is attracted to the anionic paper fibers causing co-flocculation of pigment and paper fines so as to increase pigment and paper fines retention and, additionally, optical and mechanical properties of the paper. When added to paint, the optical properties and hiding power are improved. When added to a paper furnish containing pitch, the pitch fines are absorbed.

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CATIONIC CLAYS AND USES IN PAPER AND PAINTSFIELD OF THE INVENTION

5 This invention relates to cationic clays and their use in paper and paints, and more particularly relates to cationic kaolin clays, their preparation, use as a filler in paper, as a pitch control agent in paper making, and as a coating agent in paints.

BACKGROUND OF THE INVENTION

10 It is well known to incorporate various fillers in paper and the performance of fillers varies considerably depending on the particular filler used and its characteristics. Such fillers, often called pigments, include various clays, titanium dioxide, calcium carbonate, and similar materials which provide 15 strength, opacity, brightness and other characteristics to the paper. The fillers are conventionally added to the paper furnish during preparation of the paper and are preferably uniformly distributed throughout the paper sheet to optimize the ability to scatter light.

20 The introduction of pigments conventionally often requires the use of retention aids which causes the primary particles to agglomerate and consequently decreases light scattering efficiency.

25 It has been suggested that the use of positively charged particles offer the possibility of mutual interaction with negatively charged fibers and so that such fillers would remain uniformly distributed in the

paper furnish. Retention aids, used for this purpose, are usually cationic polyelectrolytes.

5 In a publication by Alince et al Paperi ja Puu-Papper och Tra, No. 3, 1983, pages 123, 124, 125, 136, it is suggested that titanium dioxide particles will acquire a positive charge when treated with polyethylenimine and will deposit on negatively charged fibers suspended in water because of mutual attraction.

10 In a further publication by Alince et al, Tappi Journal, January 1983, pages 92-95, it is pointed out that the use of positively charged particles offers the possibility of mutual interaction with negatively charged fibers. In this paper, the behavior of kaolin clay pigments which have been treated with cationic polyelectrolytes to give them a positive charge is studied. In this study, three types of kaolin clay pigments which have different particle sizes were used and treated with low molecular weight polyethylenimine. 15 This caused the pigments to acquire a positive charge that was pH dependent. The authors concluded from this study that there is substantial potential advantage to using positively charged pigment particles in the wet-end addition because of their resulting mutual attraction to and ready deposition on negatively charged fibers. It was pointed out that in the absence of retention aids, the pigment particles are more likely to remain in the water phase, not retained with the fiber. In this case, the pigment particles are not 20 associated with the paper and, therefore, have no effect on paper properties. The authors further pointed out however that the colloidal forces between the oppositely charged surfaces of pigment particles and fibers were not strong enough to ensure an 25 irreversible deposition.

30 35 A further study on this subject was presented by John G. Penniman, President, Paper Chemistry Consulting

Laboratory, Inc., Stoneleigh Avenue, Carmel, New York, for The Third International Seminar On Paper Mill Chemistry, Boston, Massachusetts, August 30 - September 2, 1981. This paper concerned the suggested use of calcium carbonate as a cationic filler in the preparation of paper. In this paper the cationic calcium carbonate was shown to be superior to untreated calcium carbonate.

In a publication by Weigl et al, "Wochenblatt Fur Papierfabrikation", Vol. 17, p. 767-773, 1987, there is disclosure of cationic additives for coating colors. Cationic additives such as quaternary ammonium compounds, cationic PVA, and heavily degraded, low-molecular cationic galactomannans are mentioned. Calcium carbonate was used as a coating pigment and is suggested as allowing reasonable solids contents of a cationic coating color to be achieved in contrast to kaolin.

20 It is evident that the art recognizes that fillers which have a cationic charge could provide improved results when incorporated into paper during the paper making operation. The present invention provides a cationic clay which provides these improved advantages heretofore recognized by the prior art, and provides 25 the advantages of superior attraction between the anionic paper fibers and the pigment without the deficiencies of the prior art cationic pigments.

In the operation of a pulp mill in the production of paper, one of the recurring problems is control of the pitch which is deposited during the operation. Pitch is the sticky, resinous substance of varying composition which originates from the extractive fraction of wood in the paper making process. Pitch is reported to be composed of fatty acids and rosin acids and their corresponding calcium, magnesium, and sodium salts. The pitch exists in its dispersed state

until chemical changes in the paper furnish cause it to agglomerate and deposit on screens, felts or other paper machine surfaces. This results in holes or breaks in the sheet and expensive down time for clean ups. It is reported that the paper industry loses 30 million dollars annually because of lost production caused by pitch problems. Though various measures have been taken to combat these problems, by far the most effective measure taken to the present date is the use of talc to adsorb the pitch, thereby preventing agglomeration and subsequent deposition. The talc pitch complex is carried out as part of the final product so that no problem arises from its presence. There is discussion of this problem by Gill in "Pulp Processing", Vol. 48, No. 9 (August, 1974) p. 104. In addition, there is disclosed in Tappi Conference Paper: Alkaline Pulping Test 1976 a publication by Albert R. Kaiser of St. Regis Paper Company on "The Use of Talc to Control Pitch Deposition", pps. 133-134.

Use of talc as a pitch deposition control agent, however, is expensive because of the price of talc, so there is a need to increase efficiency of such pitch deposition controls, while at the same time increasing cost savings in operation of the process.

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SUMMARY OF THE INVENTION

It is accordingly one object of the present invention to provide a cationic clay which is useful as a filler in paper, as a pitch control agent in paper making, as a coating agent in paper, and as a coating agent in paints.

A further object of the invention is to provide a cationic kaolin clay which provides superior characteristics as a filler or coating agent when incorporated into a paper making operation.

A still further object of the invention is to provide a cationic kaolin clay which provides improved attraction for paper fibers including fiber fines and further provides improved optical properties including 5 brightness and printing properties to the paper and also provides improved hiding power when incorporated into paint as a coating agent.

An even further object of the invention is to provide a modified kaolin clay for use in the control 10 of pitch in paper making systems.

A still further object of the invention is to provide a modified kaolin clay which has been treated with aluminum chlorohydrate or hydrotalcite (or 15 hydrotalcite analogues which are magnesium-aluminum double hydroxides of varying $[Al]/[Al] + [Mg]$ molar ratios), which modified kaolin clay is useful in the control of pitch and simultaneously as a filler for paper when added to a paper making process.

Other objects and advantages of the present 20 invention will become apparent as the description thereof proceeds.

In satisfaction of the foregoing objects and advantages there is provided by this invention a cationic kaolin clay, said cationic kaolin clay having 25 been produced by treatment of the clay with aluminum chlorohydrate.

Also provided by the present invention is a method for the treatment of paper which comprises adding the cationic kaolin clay of this invention to the paper 30 making operation to improve fiber retention of the cationic clay to enhance the use of the clay as a filler in the paper and to control pitch deposition in the process.

The present invention also provides paper 35 containing as a filler or a coating agent and/or a pitch control agent, a cationic kaolin clay, said

cationic kaolin clay having been produced by the reaction of kaolin clay and aluminum chlorohydrate.

5 The present invention also provides a paint containing a coating agent comprising a cationic kaolin clay, said cationic kaolin clay having been produced by the reaction of kaolin clay and aluminum chlorohydrate.

10 The present invention provides a kaolin clay which has been treated with aluminum chlorohydrate or hydrotalcite or analogue, either in the dry form or slurry form, said treated kaolin clay being useful for the control of pitch deposition in a paper making process.

15 There is also provided by the present invention a method for the adsorption of pitch and thus the control of pitch deposition in a paper making process which comprises addition of an aluminum chlorohydrate-treated kaolin clay or a hydrotalcite-treated kaolin clay to the paper furnish.

BRIEF DESCRIPTION OF THE DRAWINGS

20 Reference is now made to the drawings accompanying this application wherein:

Figure 1 is a series of three graphs showing measurement of the cationicity of an untreated clay;

25 Figures 2, 3, 4, 5 and 6 are a series of three graphs having measurements of the cationicity of a kaolin clay sold commercially as Hydrasperse® by J. M. Huber Corporation, when treated with aluminum chlorohydrate at different treatment levels; and

30 Figure 7 is a graph showing a comparison of different clays and their treatment levels of aluminum chlorohydrate with respect to the amount of pitch adsorbed in a pitch control system.

DESCRIPTION OF PREFERRED EMBODIMENTS

As indicated above, this invention is concerned with the production of a modified kaolin clay and use of the modified kaolin clay as a filler and/or pitch control agent in the paper making industry and a coating agent in paints. According to this invention, it has been unexpectedly discovered that kaolin clays can be chemically modified to be made cationic so as to improve various characteristics for their use as fillers in paper as coating agents in paint and as pitch control agents in paper making processes.

In conventional use of kaolin clay in paper making, a water washed kaolin clay pigment is usually dispersed anionically to facilitate pumping, screening, slurry shipment, etc. At this point, the clay is not cationic. To accomplish attraction between anionic paper fibers and an anionic pigment such as the clay, polymeric bridging agents known as retention aids have been used. Other means to accomplish the attraction which have been used in the prior art include the treatment of one component with a highly cationic material such as modified potato starch and the other component with an anionic material such as polyacrylate or sodium silicate so that when these materials are mixed, strong attraction forces are generated. When cationicity is desired in coatings containing pigments such as kaolin clay, chemical flocculants such as quaternary ammonium salts are usually added to the coating.

According to the present invention it has been discovered that a normally anionic kaolin clay can be made cationic prior to addition to the paper furnish so as to result in improved attraction between a cationic clay filler and the fibers of the paper. This means that it may not then be necessary to add the additional agents such as polymeric bridging agents to the

5 mixture. Further it follows from previously cited work with cationized pigments that the cationic clay of this invention will provide improved attraction between the paper fibers and, as a result of improved paper formation, the cationic clay and improve printing properties of the paper. Further, when the cationic clay of this invention is incorporated into paints and paper coatings, the resulting optical properties of the paint and coating films exhibit improved brightness and
10 hiding power.

15 It has been discovered according to the present invention that the surface electrochemistry of kaolin clay is altered by the technique of treating the clay with aluminum chlorohydrate or a hydrotalcite. Unexpectedly it has been discovered that with an adequate treatment level, the cationicity is permanent across the pH range of 3-10 where virtually all paper making and coating is done. As a paper filler, the cationic clay is attracted to the anionic paper fibers rather than being repelled, as would be expected when using an anionic-dispersed clay. The attraction promotes pigment retention, which lessens or eliminates the need for retention aids, which are often high cost items.

25 Additionally, when added to an aqueous system containing anionic fibers, such as a paper fiber slurry, the cationic clay unexpectedly shows its greatest attraction for fiber fines thus causing co-flocculation of pigment and fiber fines. These flocs are more easily retained in the forming sheet than the non-flocculated fines and are therefore better removed from the white water system. In being retained, it will be seen that the fiber fines promote improved opacity and, in some instances, sheet mechanical properties. Furthermore, with more fines retained, the white water system should remain cleaner, reducing or
30
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5 eliminating the need for drainage aids. Additionally with less fines in the recirculating water, less effluent would require treatment or the amount of effluent sent for treatment would contain less solids and usually a lower BOD level.

10 In aqueous coatings such as paper coating, paint, etc., cationic clays should act to cause a controlled microflocculation of the coating ingredients particularly at the substrate-coating interface thus building structure into the coating as it begins to dry. This could be referred to as lowering the immobilization point of the coating. The results of 15 all of this would then include improving the optical properties of the coating, including brightness and hiding power.

20 In accordance with this invention it has been discovered that a kaolin clay which has been modified by treatment with aluminum chlorohydrate or a hydrotalcite will provide normally inert kaolin clay with qualities which enables the resulting modified kaolin clay to have cationic characteristics which make the modified clay eminently suitable as a filler in paper making processes and as a coating agent in 25 paints.

30 According to this invention it has also been unexpectedly discovered that kaolin clays chemically modified as described herein also improve their pitch adsorption characteristics so that they can serve as replacements for talc in the paper making industry and provide increased efficiency and cost savings.

35 In accordance with this invention it has been discovered that a kaolin clay which has been modified by treatment with aluminum chlorohydrate or a hydrotalcite will provide normally inert kaolin clay with qualities which enables the resulting modified clay to have pitch adsorption characteristics which

makes the modified clay eminently suitable as a pitch adsorption agent in paper making processes.

5 The preferred reactant is a kaolin clay but analogous substrates, either natural or synthetic, materials such as alumina trihydrate and sodium alumino silicates may be used in the invention.

10 Kaolin clays are well known materials and various kaolin clays are mined throughout the southeast and are identified, for example, by the region from which they are obtained, such as middle Georgia clays and east Georgia clays. All kaolin clays regardless of origin are considered to be useful within the scope of the present invention such as English clays, China clays, Australian clays and Brazilian clays.

15 The kaolin clay according to one embodiment of the present invention is modified by treatment with aluminum chlorohydrate. Aluminum chlorohydrate is a known material and is also referred to as an aluminum chlorohydroxide complex. It is of the formula
20 $\text{Al}_2(\text{OH})_5\text{Cl}_2\text{H}_2\text{O}$. Aluminum chlorohydrate is sold commercially under the name Chlorhydrol[®] by Reheis Chemical. As available commercially, Chlorhydrol[®] is a clear, colorless 50% solution and is preferably used in that form in this invention. However, other physical
25 forms of the aluminum chlorohydrate may also be used in treatment of the clay.

30 In the present invention the clay may be treated in dry form with the aluminum chlorohydrate or it may be treated as a slurry. It is highly preferred that the modified clay be prepared in slurry form, since test results have shown that the slurry treatment process is a more simple procedure and the nature of slurry treatment lends itself to more uniform mixtures. Thus, this represents the preferred procedure.

35 It has been discovered that both fine particle size (90-99% finer than 2 μ), high surface area (22

m^2/gm) clays and coarse particle size (80% finer than 2u or lower), low surface area clays ($12 \text{ m}^2/\text{gm}$ or less) respond equally well to treatment with aluminum chlorohydrate to produce effective cationic fillers.

5 Further, it has been found that degritted crude clays as well as fractionated and leached beneficiated clay fractions can be effectively treated with aluminum chlorohydrate to produce cationic clay products. It is preferred that crude clay or fractionated clay slurries contain a minimum amount of dispersant (preferably 0.1 - .15% of Calgon) prior to treatment with aluminum chlorohydrate, and that leached beneficiated clay fractions be treated with aluminum chlorohydrate as undispersed filter cake slurries. Further, the amount of aluminum chlorohydrate which should be used to treat the clay should range from about 0.5 to 1.5 wt.% and more preferably from about 0.75 to 1.25 wt.%. It has been found that this minimum amount of aluminum chlorohydrate is effective to modify the clay in such manner that the resulting modified clay excels as a cationic clay paper filler.

The treatment of the kaolin clay with the aluminum chlorohydrate is preferably carried out by forming a clay slurry at a solids content of about 15 to 50 wt.%, preferably 30%. Thereafter, with agitation, sufficient aluminum chlorohydrate, such as a 30 to 60 wt.% solution, and preferably a 50 wt.% solution, is added to give a total treatment level based on the clay weight of 0.5 - 1.5%, and preferably 0.75 to 1.25%. The treated slurry is then blunged for about 5 to 60 minutes, preferably 10 to 20 minutes, and then is either spray dried or filtered and either dried as a cake or reslurried at 30% solids and spray dried. It has been found that the treated slurry may be stored

for several days prior to drying without affecting the cationic properties.

5 The modified clay may also be formed from a dry clay by treatment with aluminum chlorohydrate. In this procedure, the aluminum chlorohydrate suspension is added directly to dry clay to achieve uniform and thorough mixing and a resultant moistened clay. The resultant treated clay is either oven dried or dried using a rotary dryer/flash dryer combination and milled 10 to the desired fineness of grind.

15 While either slurry treatment or dry treatment of the clays may be used, use of the slurry process is preferred since it is a comparatively simple process and the nature of slurry treatment lends itself to more uniform mixing. For these reasons, the slurry treatment is preferred.

20 In a second embodiment of the present invention, the clay may be treated with a double hydroxide of magnesium and aluminum to modify the clay. One recognized mineral form of magnesium and aluminum double hydroxide is called hydrotalcite and is of the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. The term hydrotalcite will be used to refer to the recognized mineral form as 25 well as hydrotalcite analogues which are magnesium-aluminum double hydroxides of varying molar ratios.

30 According to this invention it is preferred that the clay be treated with hydrotalcite-like materials which have been produced in-situ from aluminum chloride and magnesium chloride. In this reaction, the in situ formation of the hydrotalcite in a clay slurry is achieved by the addition of desired quantities of 1.0M $AlCl_3$ and 1.0M $MgCl_2$ to a 10 to 30 percent solids aqueous clay slurry, preferably 20% solids, and blumping to achieve good mixing. A time of about 5 to 35 15 minutes, preferably 10 minutes, is preferred. Thereafter, sodium hydroxide, such as 2M aqueous

sodium hydroxide solution, is slowly added to achieve a pH in the range of 10.0 to 11.0, preferably 10.5. The slurry is then blunged for 5 to 15 minutes and filtered as on a Buchner funnel. The filter cake is then reslurried at 20 to 40 wt.% solids, refiltered and dried at 120°C, then hammer-milled to desired fineness of grind. The treatment level will depend on the ratio of aluminum and magnesium and the percent alumina, as well as percent magnesium oxide per 100 parts of clay. The following represents a sample calculation to achieve a proper treatment level for in situ formation of the hydrotalcite.

Sample Calculation of Treatment Level for in situ Formation of Hydrotalcite

15 Treatment Level: Al/Al+Mg = .67 %Al₂O₃ = .68%

ml 1.0 M AlCl_3 added to 300 g clay = 26 g

ml 1.0 M $MgCl_2$ added to 200 g clay = 13.3

20 26.8 ml 1.0 M AlCl_3 = 26.8 m mole AlCl_3 ----- 13.4 m mole Al_2O_3

$$13.4 \text{ mole Al}_2\text{O}_3 \times 102\text{mg Al}_2\text{O}_3/\text{mmole} = 1.367\text{g}$$

$$1.367 \text{ g Al}_2\text{O}_3 / 200 \text{ g clay} = .68 \text{ g Al}_2\text{O}_3 / 100 \text{ g clay}$$

13.2 ml 1.0 M $MgCl_2$ = 13.2 m mole $MgCl_2$ ---- 13.2 ml MgO

$$13.2 \text{ m mole MgO} \times 40.3 \text{ mg MgO/m mole MgO} = .532 \text{ g}$$

$$25 \quad .532 \text{ g MgO}/200 \text{ g clay} = 0.267 \text{ g MgO}/100 \text{ g clay}$$

$$\frac{\text{g Al}_2\text{O}_3/100 \text{ g clay} \times 4000}{102} = \text{ml 1.0 M Al}_2\text{Cl}_3$$

30 g MgO/100g clay x 2000 = ml 1.0 M MgCl₂

It will be seen from this calculation that the clay is treated with an amount of hydrotalcite which can range from 0.5 to 2.0 wt. %.

As pointed out above, it has been found according to the present invention, that the cationic clay of this invention shows unexpectedly great attraction for fiber fines as well as other paper fibers which results in co-flocculation of pigment and fiber fines. The cationic clay will thus act as a self-retaining pigment and as a flocculent in paper making operations. It will act as a retention aid particularly for flocculation of fines whether they are pigment or fiber. It is further useful as a drainage aid in the paper making system to aid water removal or in effluent or white water treatment to reduce suspended solids. It is also useful as a clarifying agent to attract suspended or dissolved anionic materials in the system. Further it can be used as a coating pigment in paints or paper coatings to induce controlled micro-flocculation as the coating dries and thereby enhance coating efficiency.

In the Figures, the graphs in the upper left portion illustrate the zeta potential of the cationic clay of the invention.

When used as a filler in the production of paper, it is preferred to add the cationic clay to the paper furnish in amounts ranging from about 2 to 600 pounds of cationic clay per ton of dry fiber. A more preferred range of filler to be added is from about 5 to 35 pounds of cationic clay per ton of dry fiber. When used as a paper coating agent, the cationic clay can constitute up to 100% of pigment used and may be added in amounts ranging from about 2 wt. % for paper board up to about 30 wt. % of the weight of the sheet for publication paper, based on the total weight of the

sheet. When used in paints, the clay should be added in an amount of about 1 to 10 wt. %.

The results of laboratory tests indicate that clay modified with aluminum chlorohydrate or hydrotalcite have pitch adsorption qualities equal to, and in most cases superior to, those of the more expensive talc. Thus, an aluminum chlorohydrate-kaolin combination was found to adsorb up to 96.25% of the synthetic pitch in test systems, as compared to a 35-45% adsorption by talc. The treated clay performed satisfactorily in paper filler applications. Chemical modification of the clay slurry using the in situ formation of hydrotalcite was also shown to be effective in pitch adsorption. However, the aluminum chlorohydrate treatment is more preferred in this invention since hydrotalcite modified clays appeared to provide less consistent results than the aluminum chlorohydrate modification. Also, the hydrotalcite modification involves a multistep process, which is less economic than the aluminum chlorohydrate.

In order to evaluate the modified clay as a pitch control agent, test procedures were utilized to evaluate the pitch adsorptive capacity of the agents. This laboratory evaluation allowed direct measurement of adsorbed pitch on the test samples. The adsorbed pitch was extracted from the modified clays and reacted to form a colored pitch complex whose concentration could be measured spectrophotometrically. The results were reported as percent of total amount of pitch adsorbed and were compared with the 45% adsorptive capacity exhibited by talc. The method of evaluation of the pitch adsorptive capacities of mineral powders was a variation of a procedure outlined by D. A. Hughes in Tappi Conference Papers, Vol. 60, No. 7, p. 144-146 (1977), the disclosure of which is incorporated herein by reference. This involves the

mixing of a known quantity of a synthetic pitch with a dilute mineral solution. The mineral and any adsorbed pitch is then separated by centrifugation. The liquid fraction is discarded while the mineral powder is 5 dried. A solvent reagent is then added to the dry mineral to extract the adsorbed pitch which may be present. The pitch is then quantified colorometrically. In general, the results indicated that Mistron vapor talc adsorbs about 40-45% of the 10 synthetic pitch, untreated kaolin clay adsorbs less than 1%, and aluminum chlorohydrate-modified clay adsorbs up to 96.25%, so that the effectiveness of the aluminum chlorohydrate treated clay is clearly apparent. This is shown in Figure 7 accompanying the 15 application where HSP, HP, HG and Omnilfil are as defined in the examples.

It is a feature of the invention that the cationic clay may be added to the paper furnish to serve both as a pitch control agent and as a paper filler or coating 20 agent. The pitch control agent absorbs pitch fines so they do not interfere in the paper making process and can be carried into the final paper product without adversely affecting the paper. Accordingly, the cationic clay of this invention can unexpectedly serve 25 dual purposes when incorporated into a paper furnish, i.e., as a pitch control agent and filler. When used as a pitch control agent, the amount of cationic clay to be added is in the range of about 3-4 wt.% based on the total fiber in the pulp. When used as a filler, a 30 preferred range is from about 5-35 pounds of cationic clay per ton of dry fiber. Accordingly, when added in the larger amounts, the cationic clay will act as a filler and inherently act as a pitch control agent if pitch fines are present.

35 The following examples are presented to illustrate the invention. However the invention is not to be

considered to be as limited thereto as obvious variations thereon will become apparent to those skilled in the art. In the examples and throughout the specification, parts are by weight unless otherwise indicated.

5 In certain of the following examples, the clays to be treated are referred to by the tradenames Hydrasperse®(HSP), Hydraprint®(HP), Hydragloss®(HG), Hydrafine®(HF), and Omnifil®. These terms are 10 trademarks of the J. M. Huber Corporation for the types of clays utilized. The aluminum chlorohydrate used in the examples was a colorless 50% aqueous solution obtained from Reheis Chemical under the trademark Chlorhydrol®.

15 Example 1

A crude kaolin clay from Twiggs County, Georgia, was degritted and classified to a #2 grade fraction, bleached, coagulated, and filtered. The filter cake was reblunged at 30% solids with no dispersant added. 20 To this slurry, a 50 wt. % solution of aluminum chlorohydrate was added at the ratio 19 pounds of aluminum chlorohydrate per dry ton of clay under sufficient agitation to maintain good mixing. The resultant material was then spray dried at an inlet 25 temperature of 1000°F and an outlet temperature of 250°F. A control sample was also prepared by completing all the steps referred to except that aluminum chlorohydrate was not added. Surface potential measurements of the products in a water 30 slurry were obtained across the pH range of 4-10. Zeta potential measurements are shown in accompanying Figure 1 for the control clay and the treated clay, respectively. A comparison of the graphs in Figure 1 shows the cationicity of the aluminum chlorohydrate- 35 treated clay as compared to the control. In the

graphs, the units in the y axis are mPa*M/V or milliPascals times amplitude divided by voltage.

Example 2

5 A sample of paper pulp was obtained from the headbox of a paper machine which produces kraft medium paper using a furnish of approximately 60% kraft pulp and 40% recycled corrugated containers. Stock freeness
10 was determined using a Canadian Standard Freeness Tester in accordance with TAPPI Method T-227, and fines retention was measured using a Britt Jar in accordance with TAPPI Methods T-261 and T-269. Untreated clay and clay treated with aluminum chlorohydrate in accordance with Example 1 was added at proportions of 5, 10 and 20
15 pounds per ton of dry fiber to portions of the pulp, and freeness and fines retention were determined. This data is set forth in the following Table I. As will be noted from Table I, the data shows that untreated clay does not perform any function while the treated clay
20 provides fines retention and increases freeness as a result of the cationic nature of the clay.

TABLE I

| | | No Addition | 5#/T | 10#/T | 20#/T |
|---------------------------|----------------|----------------|------|-------|-------|
| FREENESS, CSF | | | | | |
| 5 | Untreated Clay | | 330 | 332 | 335 |
| | Treated Clay | 333 | 359 | 365 | 376 |
| FINES RETENTION, % | | | | | |
| 10 | Untreated Clay | | 16.0 | 15.4 | 15.8 |
| | Treated Clay | 15.7 | 29.8 | 36.4 | 44.5 |

Example 3

The cationicity of clays was evaluated using a clay which is available commercially under the trademark Hydrasperse from the J.M. Huber Corporation. This commercial grade clay was evaluated for its cationic nature as an untreated clay, as a clay which had been treated with five pounds of aluminum chlorohydrate per ton, as a clay which had been treated with 14 pounds of aluminum chlorohydrate per ton, as a clay which had been treated with 19 pounds of aluminum chlorohydrate per ton, as a clay which had been treated with 25 pounds of aluminum chlorohydrate per ton, and as a clay which had been treated with 30 pounds of aluminum chlorohydrate per ton. The evaluation was a measurement of surface potential of the products in a water slurry across the pH range of 4-9. The results are shown in Figures 2, 3, 4, 5 and 6 which are graphs from a Matec ESA Zeta potential meter. The graph of particular interest is the graph in the upper left of the page which plots zeta potential along the vertical axis and solution pH along the horizontal axis. The

point where cationicity is first obtained lies between 5 and 14 pounds per ton treatment level. At 14 pounds per ton treatment and above, the pigment remains cationic through the pH range of 4-9.

5 In graphs of Figures 1 to 6, the horizontal axis is pH value ranging from 2-12. In each case, the vertical axis is the zeta potential. Note that the units on the vertical axis change from graph to graph, from strongly electronegative (anionic) to strongly 10 electropositive (cationic).

Figure 1 - -20 to 0, always anionic (minimum is -7).

15 Figure 2 - -8 to 0, 5#/ton treatment, always anionic, but less in magnitude (-3.5).

Figure 3 - 0 to +8, 14#/ton treatment, at a pH of 9, system becomes cationic and remains so through pH 4 (+6).

20 Figure 4 - 0 to +10, 19#/ton treatment, always cationic (+8).

Figure 5 - 0 to +20, 25#/ton treatment, always cationic, but stronger in magnitude (+14).

25 Figure 6 - 0 to +25, 30#/ton treatment, always cationic, but again stronger charge (+20 at pH 4.0).

30 In the following examples, the effectiveness of pitch control powders was evaluated by permitting contact between specially prepared synthetic pitch and the pitch control powder in an aqueous system. The adsorbed pitch was extracted from the powder and quantified colorimetrically. It is difficult to extract actual pitch from a problem area in a paper mill and utilize that pitch for evaluation, so that 35 synthetic pitch was prepared from actual components of

typical pitch. The experimental procedure of the pitch preparation and evaluation involved preparing a synthetic pitch sample by combining 0.65 grams of ground gum rosin and 0.35 grams of tall oil in an 5 Erlenmeyer flask. The oily mixture was then stirred with a glass stirring rod while 1M potassium hydroxide was added dropwise until saponification resulted. Denatured ethanol (250 ml) was added to dissolve the synthetic pitch. The resulting 10 concentration of the pitch preparation is 4 mg/ml.

The pitch adsorption test procedure comprised slurring 10 grams of the test clay in a Waring blender with 400 ml distilled water for 10 minutes. 35 ml of distilled water was first added to 50 ml glass 15 centrifuge tubes, followed by 1 ml of the synthetic pitch preparation, and lastly 10 ml of the clay slurry. The mixture was then stirred with a stirring rod for 15 seconds and centrifuged for 20 minutes at 2500 rpm. The supernatant was then poured off and discarded and 20 the tube containing the mineral powder and adsorbed pitch was dried overnight at 60°C.

After drying, 10 ml of chloroform-acetic anhydride (1:1) reagent was added to the tube and stirred to release the adsorbed pitch from the mineral powder. 25 The mixture was then centrifuged for 20 minutes so that the clear reagent remained at the top of the tube. The clear reagent was poured off into a small beaker and 10 drops of concentrated sulfuric acid added to effect a color change. After exactly four minutes, the liquid 30 was measured on a spectrophotometer set at 400 nm and the absorbance value was compared to absorbance values of known quantities of extracted pitch.

Example 4

A fine particle size east Georgia crude clay 35 having a particle size of about 90% finer than two

microns was slurried as approximately 40% solids using 0.15% by weight sodium hexametaphosphate as the dispersant. The dispersed slurry was degritted on a 325 mesh screen and the degritted slurry divided into 5 eight equal samples. Chlorhydrol was added to the samples at levels ranging from 0.8 to 1.4% by weight active Chlorhydrol[®] to weight of clay. The control sample contained no Chlorhydrol[®]. Each treated sample was mixed for three minutes under low shear using a 10 dispersator equipped with a cowles type blade. The treated samples were dried on a teflon coated pan, milled, and evaluated for pitch adsorption characteristics using the modified Hughes method. Results of the tests are given in Table II.

15

TABLE II

Effect of Chlorhydrol[®] on Pitch Adsorption of Treated
East Georgia Degritted Clay

| | <u>Treatment Level lbs/t Chlorhydrol[®]</u> | <u>Percent Pitch Adsorbed</u> |
|----|--|-----------------------------------|
| 20 | 0 | 10.0 |
| | 16 | 93.75 |
| | 18 | 96.25 |
| 25 | 20 | 93.75 |
| | 22 | 92.50 |
| | 24 | 90.0 |
| | 26 | 88.75 |
| | 28 | 22.50 |
| | Mistrion Vapor Talc | 45.0 |

30

The results show maximum pitch adsorption at 0.9% Chlorhydrol[®] with values decreasing with higher and lower Chlorhydrol[®] levels. In comparison the untreated clay sample showed 10.0% pitch adsorption while a Mistrion Vapor talc showed 45.0% adsorption.

Example 5

An undispersed leached filter cake sample of a middle Georgia clay having a particle size of about 82-84% finer than 2 microns was obtained for treatment 5 with Chlorhydrol®. An undispersed slurry was prepared from the filter cake at 30% solids by adding water to the filter cake while mixing under moderate shear. The slurry was divided into eight equal portions and treated with Chlorhydrol® in the same manner as Example 10 4.

TABLE III

Effect of Chlorhydrol[®] on Pitch Adsorption of Treated
Hydrasperse[®] Filter Cake

| | <u>Treatment Level lbs/t Chlorhydrol[®]</u> | <u>Consistency of Treated Slurry</u> | <u>Percent Adsorbed</u> |
|---|--|--|-----------------------------|
| 5 | 16 | Very thick | 75 |
| | 18 | Thick | 80 |
| | 20 | Slightly Thick | 79 |
| | 22 | Slightly Fluid | 35 |
| | 24 | Moderately Fluid | 17.5 |
| | 26 | Fluid | <10 |
| | 28 | Quite Fluid | <10 |

Results of the test given in Table III show a maximum adsorption of a treatment level of 18 lbs./t decreasing drastically at levels above 20 lbs./t. In comparison the untreated control had less than 10% pitch adsorption and Mistron Vapor had 45% pitch adsorption. The results would indicate that the coarser particle size middle Georgia clays are more sensitive to overtreatment than the fine particle east Georgia clays.

Example 6

A degritted east Georgia clay slurry was prepared in the same manner described in Example 4. The slurry was divided in half and each half treated with 1% Chlorhydrol[®]. One-half was mixed for about 15 minutes and spray dried. The second-half was filtered on bottle filters, placed in a forced air oven and dried. Both samples were evaluated for pitch absorption by the modified Hughes method.

The results shown in Table IV indicate that some Chlorhydrol[®] was lost during the filtration but that the resulting pitch adsorption of the treated clay was

still substantially higher than the value for talc while lower than the value for the unfiltered sample.

Example 7

5 An unbeneficiated Hydrasperse® slurry prepared from middle Georgia crude clay and having a particle size of about 84% minus two microns was obtained and treated in the same manner as described in Example 6. Pitch adsorption characteristics as determined by the Modified Hughes method is given in Table IV.

TABLE IVEffect of Filtering Treated Slurry on Pitch Adsorption
of East Georgia Clay

| 5 | <u>Example</u> | <u>Percent Pitch Adsorbed</u> | | |
|---|-------------------------------------|-------------------------------|-----------------|-------------------|
| | | <u>Spray Dried, As Is</u> | <u>Filtered</u> | <u>Oven Dried</u> |
| | Omnifil® (Example 3) | 82.5 | | 73.0 |
| | Hydrasperse® (Example 4) Georgia | 66.0 | | 47.5 |

10 The filtered middle Georgia sample had a pitch adsorption value significantly lower than the unfiltered control indicating a substantial loss of treating chemical. The pitch adsorption value was still equivalent to talc which has a pitch adsorption 15 capacity of about 35-45%. The decrease in pitch adsorption due to filtration was greater for the middle Georgia clay than for the east Georgia clay.

Example 8

20 A leached Hydragloss® clay sample was obtained as filter cake from the rotary vacuum filter and the filter cake reslurried at 25% solids and divided into two samples. The first sample was treated with 20.0 lbs./t of Chlorhydrol® to produce a flowable slurry and spray dried. The second sample was first dispersed 25 with 0.15% of sodium hexametaphosphate dispersant (available commercially as Calgon Dispersant), and then treated with 20 lbs./t of Chlorhydrol® before spray drying. The pitch adsorption characteristics of the two samples determined by the modified Hughes 30 method are given in Table V.

TABLE V

Treatment of Hydragloss[®] Filter Cake with Chlorhydrol[®]

| 5 | <u>Sample</u> | <u>Calgon</u> | <u>Chlorhydrol[®]</u> | <u>Slurry</u> | <u>Pitch</u> |
|---|---------------|------------------------|--------------------------------|---------------|------------------------|
| | | <u>Dispersant</u> % | <u>%</u> | | <u>Adsorption</u> % |
| | 1 | --- | 1.0 | fluid | 82.5 |
| | 2 | .15% | 1.0 | thick | 69.0 |

10 The results show that good pitch adsorption characteristics can be obtained by treating reslurried filter cake with sufficient Chlorhydrol[®] to obtain a good slurry flow or by treating dispersed filter cake slurry with Chlorhydrol[®].

Example 9

15 A crude east Georgia Clay was obtained and dispersed at about 40% solids using sodium hexameta-phosphate as the dispersant. Dispersant levels of 2, 4, 6 and 8 lbs./t of clay were employed. The dispersed slurries were degritted and solids reduced to 25%. Each slurry was then treated with 20 lbs./t of active 20 Chlorhydrol[®] and pan dried. Pitch adsorption for the four samples, as determined by the modified Hughes method is given in Table VI.

TABLE VI

Effect of Dispersant on Pitch Adsorption of Degritted East Georgia Clay

| | <u>Dispersant Level,</u> <u>% Calgon</u> | <u>Slurry</u> <u>Consistency</u> | <u>Pitch Adsorption,</u> <u>%</u> |
|----|---|-------------------------------------|--------------------------------------|
| 30 | .10 | Moderately Fluid | 82.5 |
| | .20 | Moderately Thick | 85.0 |
| | .30 | Thick | 82.5 |
| | .40 | Very Thick | 75.0 |

Very little difference in pitch absorption was observed for the four samples, however, the lower level of dispersant would be preferred. A difference in the consistency of the treated slurries was observed with 5 the sample containing the least amount of dispersant being the most fluid and the sample containing the greatest amount of dispersant being the most viscous.

Example 10

10 A coarse centrifuge underflow fraction from a middle Georgia clay having a particle size of 30% minus 2 microns and a surface area of $8.5 \text{ m}^2/\text{gm}$ was treated with from 8 to 21 lbs. Chlorhydrol[®] per ton of clay and the treated slurries pan dried. The pitch adsorption characteristics of the treated clays are given in Table 15 VII.

Maximum pitch adsorption was obtained with 15 lbs./t of Chlorhydrol[®], indicating that a suitable pitch adsorption product could be produced from a coarse underflow fraction.

20 Example 11

Leached Hydraprint[®] filter cake, which is a delaminated clay produced from middle Georgia clays, was treated with Chlorhydrol[®] at 30% solids and spray dried. The Hydraprint[®] fraction had a surface area of 25 $11.3 \text{ m}^2/\text{gm}$ and a particle size of 72% minus 2 microns. Results of the test are given in Table VII.

TABLE VII

Pitch Adsorption of Treated Underflow Clay

| Clay | Chlorhydrol [®] , lbs./t | Pitch Adsorbed, % |
|------|--------------------------------------|----------------------|
| 5 | Centrifuge | 8 |
| | Underflow | 12 |
| | Underflow | 15 |
| | Underflow | 18 |
| | Underflow | 21 |
| 10 | Hydraprint [®] | 15 |
| | Hydraprint [®] | 18 |
| | Hydraprint [®] | 21 |
| | Hydraprint [®] | 21 |

The results of the test indicated good pitch adsorption characteristics at a treatment level of 18 to 21 lbs./t.

Example 12

A degritted east Georgia clay slurry was treated with Chlorhydrol[®] at levels ranging from 5 to 18 lbs./ton of clay. The treated slurries were pan dried and evaluated for pitch adsorption characteristics using the modified Hughes method. Results of the tests are given in Table VIII.

TABLE VIIIPitch Adsorption of East Georgia Clay Treated With Different Levels of Chlorhydrol[®]

| | Chlorhydrol [®] , lbs./t | Pitch Adsorption, % |
|----|--------------------------------------|------------------------|
| 30 | 5 | 10 |
| | 10 | 37.5 |
| | 12 | 74 |
| | 15 | 78 |
| | 18 | 75 |
| | 20 | 82.5 |

The results indicate that good pitch adsorption

characteristics can be obtained by treating degritted east Georgia clays with as little as 12 lbs./t of Chlorhydrol® but that maximum adsorption is obtained with at least 20 lbs./ton.

5 Example 13

An undispersed middle Georgia Hydrasperse® fraction was treated with 18 lbs./t of Chlorhydrol® and pan dried in an aluminum electric frying pan as well as a teflon coated pan. The slurries were dried to about 10 5% moisture and then to dryness in an oven. The sample dried in the uncoated pan had a pitch adsorption value of 69% while the sample dried in the teflon coated pan had a value of 80%, indicating that the Chlorhydrol® interacted with the aluminum during drying.

15 Example 14

A fine particle, high surface area airfloated clay from South Carolina was treated neat with Chlorhydrol® using a Vee Blender. The treated clay products containing 0.75, 1.0 and 1.5% Chlorhydrol® were oven dried, milled and evaluated for their pitch adsorption capabilities using the modified Hughes method. The samples treated with .75, 1.0 and 1.5% Chlorhydrol® gave pitch adsorption values of 85, 24 and 20% respectively. The sample tested with 0.75% Chlorhydrol® had a pitch adsorption capacity of about 25 twice that of talc.

Example 15

The in situ formation of hydrotalcite in clay slurries was most successful for pitch control when 30 utilizing undispersed starting clays. In this example a study was conducted of hydrotalcite formation in a

5 predispersed Hydrafine® slurry prepared from production spray dried clay, as well as both dispersed and undispersed slurries prepared in the laboratory from undried Hydrafine® filter cake. While production Hydrafine® and the dispersed Hydrafine® filter cake produced similar results of 28.75 and 30% adsorption, respectively, the undispersed Hydrafine® produced 42% adsorption levels. These results are shown in the following Table IX.

TABLE IX
Hydrotalcite

| | <u>Clay</u> | <u>Al/Al+Mg</u> | <u>% Al₂O₃</u> | <u>% MgO</u> | <u>% Pitch Adsorbed</u> | |
|----|----------------------------|-----------------|--------------------------------------|--------------|-------------------------|-------------------------|
| 5 | Hydrafine® Production | .46 | 1.02 | 1.0 | 28.75 | Production |
| | Hydrafine® | .44 | 1.02 | 1.0 | 30 | Dispersed, treated |
| 10 | Filter cake undispersed | .44 | 1.02 | 1.0 | 42 | Undried, undispersed |
| | | .44 | 1.02 | 1.0 | 42 | Dried |

Example 16

15 A similar test with production Hydraprint® along with Hydraprint® filter cake collected from the plant was conducted. In this test, treated Hydraprint® from production exhibited a 35% adsorption capacity, while the dispersed filter cake yielded a 30% adsorption value. Undispersed treated Hydraprint® filter cake provided 41% adsorption. These results are shown in the following Table X.

TABLE X
Hydrotalcite

| | <u>Clay</u> | <u>Al/Al+Mg</u> | <u>% Al₂O₃</u> | <u>% MgO</u> | <u>% Pitch Adsorbed</u> | |
|----|----------------------------|-----------------|--------------------------------------|--------------|-------------------------|-----------------------|
| 25 | Hydraprint® Production | .44 | 1.02 | 1.0 | 35 | Production |
| | Hydraprint® | .44 | 1.02 | 1.0 | 30 | Dispersed, treated |
| 30 | Filter cake undispersed | .44 | 1.02 | 1.0 | 41 | Dried, |

Example 17

5 The treatment of dispersed clays with hydrotalcite was found to be less effective than treatment of clays devoid of dispersants. It was found that the dispersion of previously treated clays rendered the once effective pitch control clay with essentially no adsorptive capacity. The Hydrasperse® filter cake treated with the hydrotalcite adsorbed 47.5% of the pitch in test systems, but the addition of dispersant 10 destroyed the adsorptive capacity of the product. These results are shown in Table XI, which is as follows:

TABLE XI
Hydrotalcite

| 15 | <u>Clay</u> | <u>Al/Al+Mg</u> | <u>% Al₂O₃</u> | <u>% Mgo</u> | <u>% Pitch Adsorbed</u> | |
|----|-----------------------------|-----------------|--------------------------------------|--------------|-------------------------|----------|
| | Hydrasperse® undisperser | .44 | 1.02 | 1.0 | 47.5 | Treated, |
| | Filter cake (control) | | | | 0 | |

Example 18

20 In order to evaluate the effectiveness of the Chlorhydrol® and hydrotalcite treatment, treatments with other compounds were carried out. In these treatments, the Hydragloss 90® and Omnifil® clays were 25 treated with octyl, methyl, vinyl and monoamino silanes by dry mixture. The only silane treatment that yielded any adsorption was the octyl silane. On Hydrasperse® clay, the adsorption value is 20%, while on Omnifil® and Hydragloss 90® clays, the adsorption 30 values were 17.5 and 12%, respectively. These low values were not considered competitive in the market.

Example 19

Treatments with other compounds for comparison purposes are listed in Table XII. In this work a Hydrasperse® slurry was treated with the materials 5 listed in the Table. From the Table it will be noted that the treatment of the Hydrasperse® with alum yielded 43.75% adsorption. However, alum was not considered as a candidate for treatment of the clay for 10 pitch control because it is used as a pitch control agent alone, and in conjunction with other chemicals for pitch control in the absence of clay.

In the other examples, kaolin clay was treated with zinc chloride and sodium hydroxide in quantities 15 to form monohydroxy zinc, Zn(OH)^+ , for cation exchange bonding to the clay surface. The treatment yielded 45% pitch adsorption.

Most of the other materials reacted with the clay did not provide any pitch adsorption. The last three examples in Table XII involved treatment of Omnifil® 20 with 3-MeQMBHT and Araquad quaternary amines. Good adsorption values were realized. However, these quaternary treated products were very hydrophobic and were incompatible with water systems. Therefore, no further consideration was given to this method of 25 treatment. Table XII is as follows:

TABLE XII
Other Treatments

| <u>Clay</u> | <u>Treatment Type</u> | <u>% Pitch Adsorbed</u> |
|----------------|--------------------------------|-----------------------------|
| 5 Hydrasperse® | Alum | 43.75 |
| | Al-acetate | - |
| | ZnO | - |
| | Mg. Silicate | - |
| | ZnCl ₂ | - |
| | Al ₂ O ₃ | - |
| | Zn(OH) ⁺ | 45 |
| | Mirapol A15 | - |
| | NiSO ₄ | - |
| | NiCl ₂ | - |
| | U-care Polymer JR-125 | - |
| | JR-400 | - |
| | MB2HT | 46.25 |
| | Araquad 12-50 | 35 |
| | Al formate | 16.75 |

Example 20

Samples of Chlorhydrol®-treated clay and hydrotalcite-treated clays with exceptional pitch adsorption capabilities were submitted to the paper testing laboratory for evaluation in filler applications. The evaluation demonstrated that the pitch control clays were acceptable in paper filler applications. The specific results are set forth below. In these studies, the Chlorhydrol® treated clay was a degritted east Georgia crude clay slurry (Area W) treated with 1.0 wt.% of Chlorhydrol®. The hydrotalcite was a Hydrafine® clay, wherein the undispersed, undried filter cake was treated with hydrotalcite formed in situ using 1.02% Al₂O₃ and 1.0% MgO. These results are as follows:

TABLE XIII

Evaluation of Optical Properties of Filled Paper Using
Clays Modified for Pitch Control

Handsheets were prepared from the following furnish:

| | | |
|----|----------------|---|
| 20 | Pulp | 70% Groundwood 30% Bleached Softwood Kraft |
| | Freeness | Kraft to 400 CSF, then blend with Groundwood |
| | pH | Alum to pH 4.5 |
| 25 | Retention Aid | Betz 1260, 0.025% on furnish |
| | Filler Loading | 2.5, 5 and 10% |
| | Basis Weight | 50g/m (40#/ream) |

RESULTS:

which illustrates that the invention can be carried out on a large scale for commercial use.

5 The invention has been described herein with reference to certain preferred embodiments. However, as obvious variations thereon will become apparent to those skilled in the art, the invention is not to be considered as limited thereto.

10 The invention has been described herein with reference to certain preferred embodiments. However, as obvious variations thereon will become apparent to those skilled in the art, the invention is not to be considered as limited thereto.

What is Claimed Is

1. A cationic kaolin clay, said cationic kaolin clay comprising kaolin clay which has been treated with a member selected from the group consisting of aluminum chlorohydrate and a double hydroxide of magnesium and aluminum.
5
2. A cationic kaolin clay according to claim 1 wherein the clay has been treated with from 0.5 to 1.5 wt. % of the aluminum chlorohydrate or double hydroxide of magnesium and aluminum.
3. A cationic kaolin clay according to claim 1 wherein the kaolin clay is treated with the aluminum chlorohydrate by forming a slurry of the kaolin clay and then reacting the slurry with an aqueous suspension of aluminum chlorohydrate in sufficient amounts to provide a kaolin clay product containing 0.5 to 1.5% aluminum chlorohydrate.
5
4. A kaolin clay according to claim 1 wherein the kaolin clay is treated with the double hydroxide of magnesium and aluminum known as hydrotalcite, the hydrotalcite being formed in situ by the reaction of aluminum chloride, magnesium chloride and sodium hydroxide.
5. A cationic kaolin clay according to claim 1 wherein the cationic kaolin clay is prepared by dry mixing the clay with an aluminum chlorohydrate aqueous suspension to provide the aluminum chlorohydrate level of 0.5 to 1.5 wt. % of the clay.
5
6. A cationic kaolin clay according to claim 5 where the treated kaolin clay is then separated from

the aqueous liquids and spray dried to provide the cationic kaolin clay.

7. Paper containing as a filler, a cationic kaolin clay of claim 1.

8. A paper according to claim 7 wherein the paper contains about 5 to 50 pounds of the cationic clay per ton of fiber.

9. A cationic kaolin clay according to claim 7 wherein the clay has been treated with from 0.5 to 1.5 wt. % of aluminum chlorohydrate.

10. A paper according to claim 7 wherein the cationic kaolin clay is prepared by treating kaolin clay with the aluminum chlorohydrate by forming a slurry of the kaolin clay which is then reacted with an aqueous suspension of aluminum chlorohydrate in sufficient amounts to provide a kaolin clay product containing 0.5 to 1.5% aluminum chlorohydrate, or by dry mixing the clay with an aluminum chlorohydrate suspension to provide the aluminum chlorohydrate level of 0.5 to 1.5 wt. % of the clay.

12. Paper containing as a coating agent, a cationic kaolin clay of claim 1.

13. A paper according to claim 12 wherein the paper contains about 2 to 30 wt. % of the cationic clay based on the total weight of the sheet.

14. A paper according to claim 13 wherein the clay has been treated with from 0.5 to 1.5 wt. % of aluminum chlorohydrate.

15. A paper containing as a filler and pitch control agent, a cationic kaolin clay of claim 1.

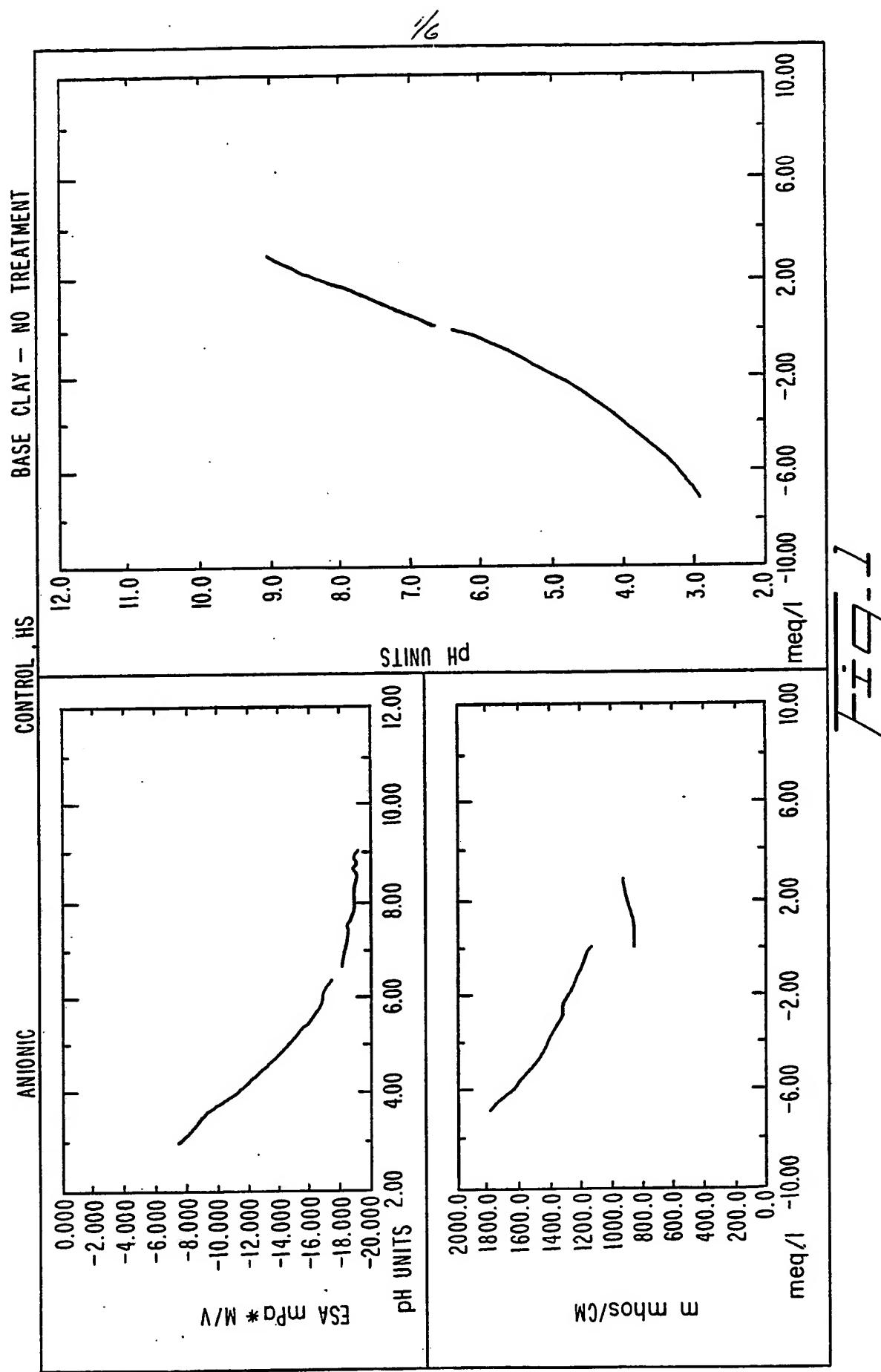
16. A method for treating paper to improve opacity which comprises adding to a paper furnish a cationic clay pigment of claim 1, the opacity being improved by coflocculation of the cationic clay pigment and paper fiber fines.

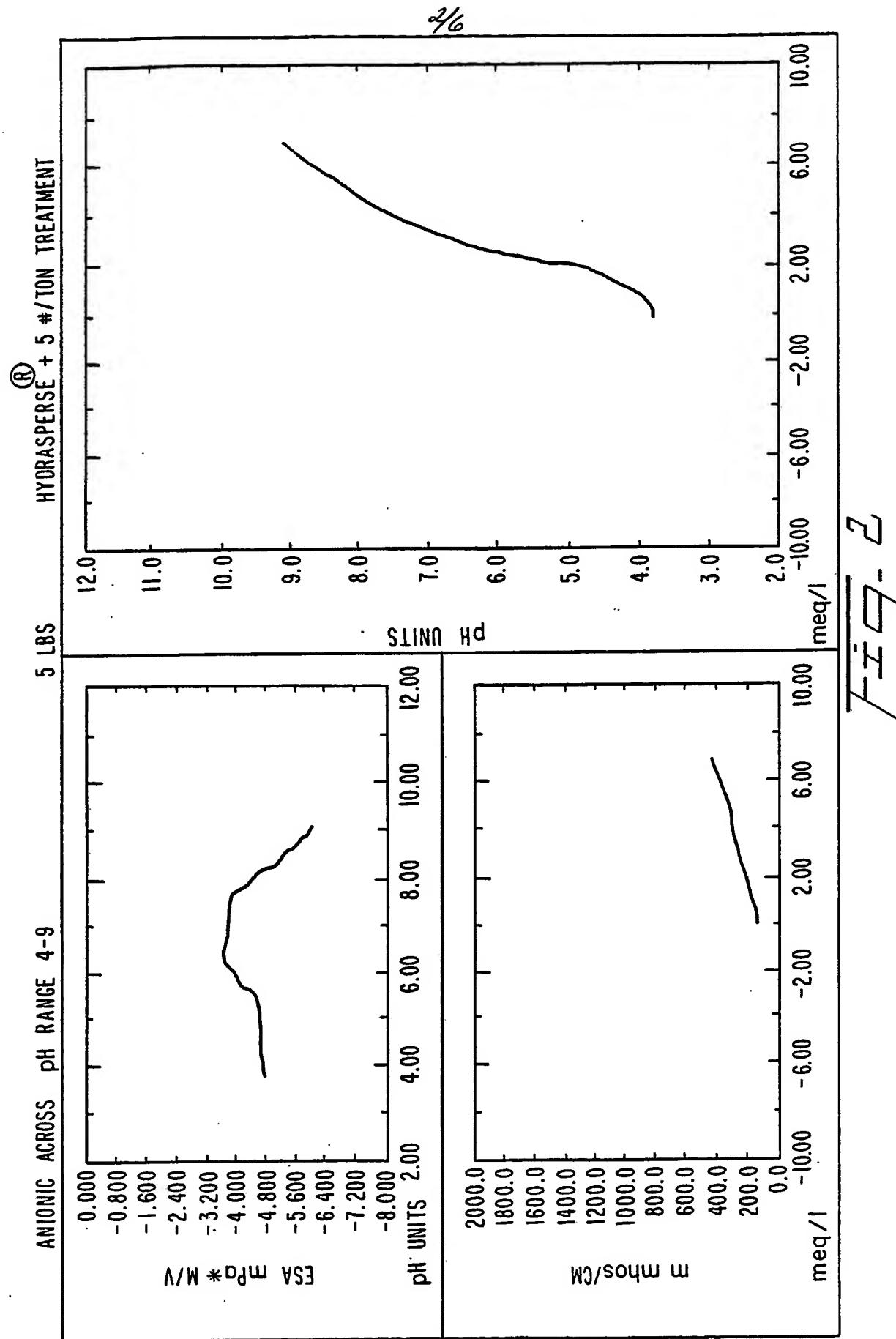
5 17. Paint containing as a coating aid, a cationic kaolin clay of claim 1.

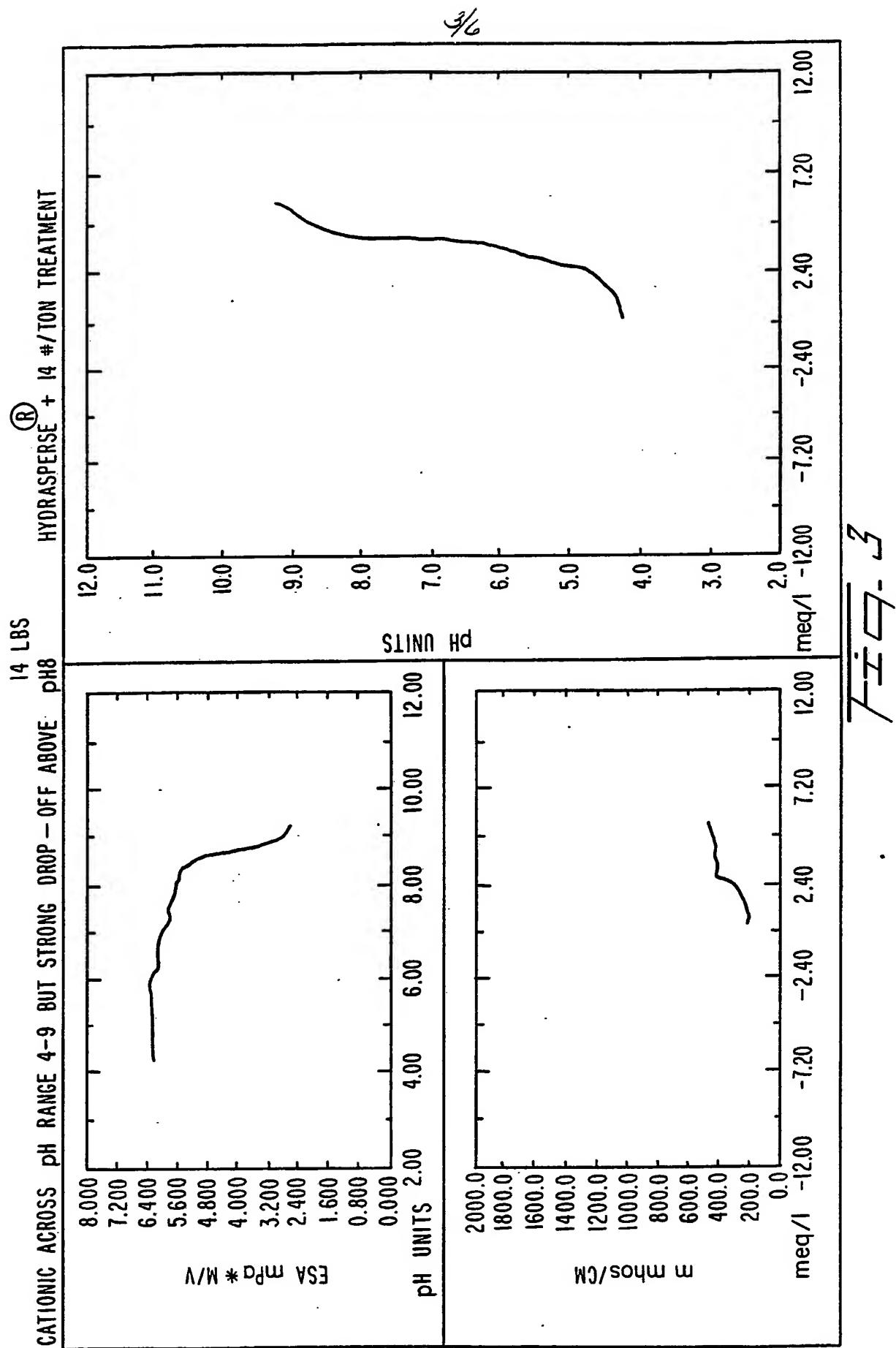
18. A paint according to claim 17 wherein the clay has been treated with from 0.5 to 1.5 wt. % of aluminum chlorohydrate.

19. A method for the adsorption of pitch in a paper making process which comprises addition to the paper furnish of a cationic clay of claim 1.

5 20. A method according to claim 19 wherein up to 75% of the pitch in the paper furnish is adsorbed by the aluminum chlorohydrate treated kaolin clay or hydrotalcite- treated kaolin clay.

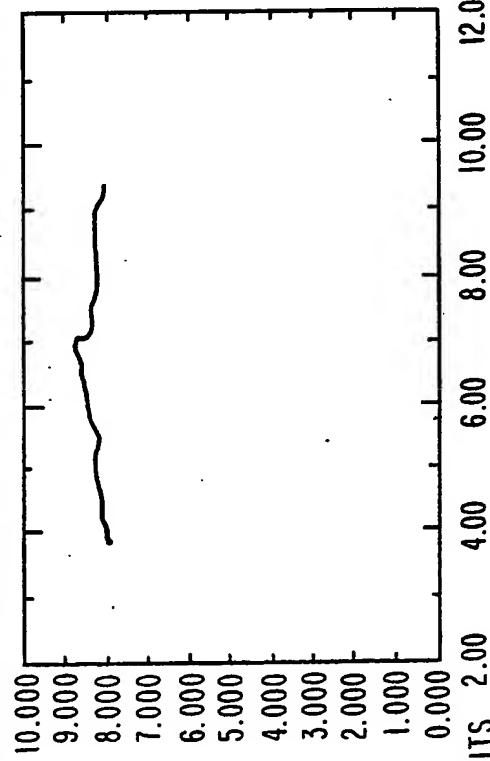






CATIONIC ACROSS pH RANGE 4-9

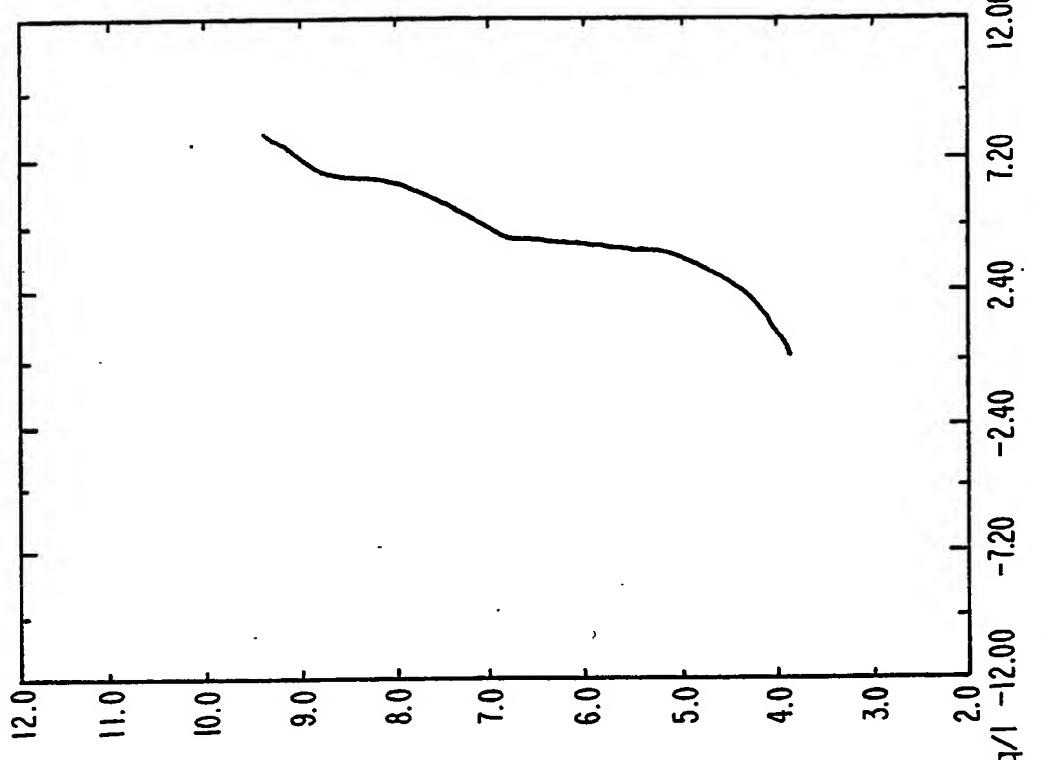
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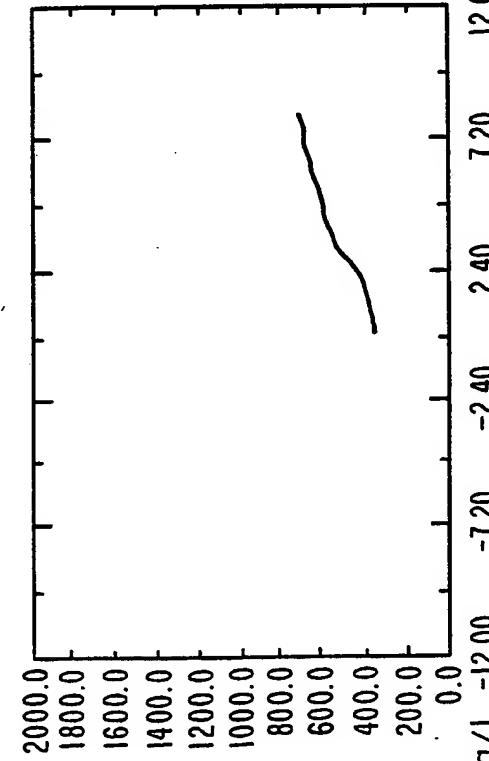
⑧ HYDRASPERSE® + 19 #/TON TREATMENT

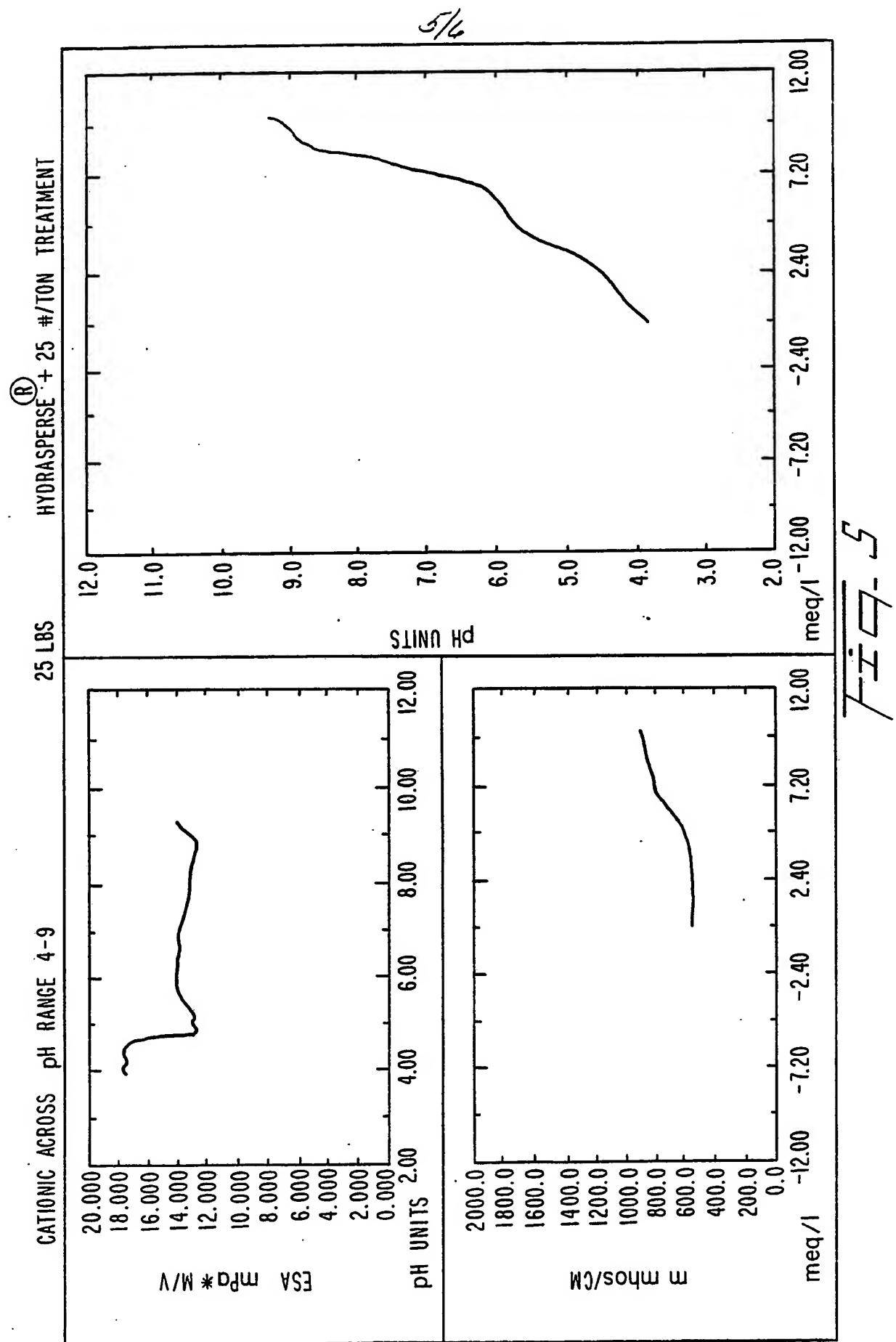
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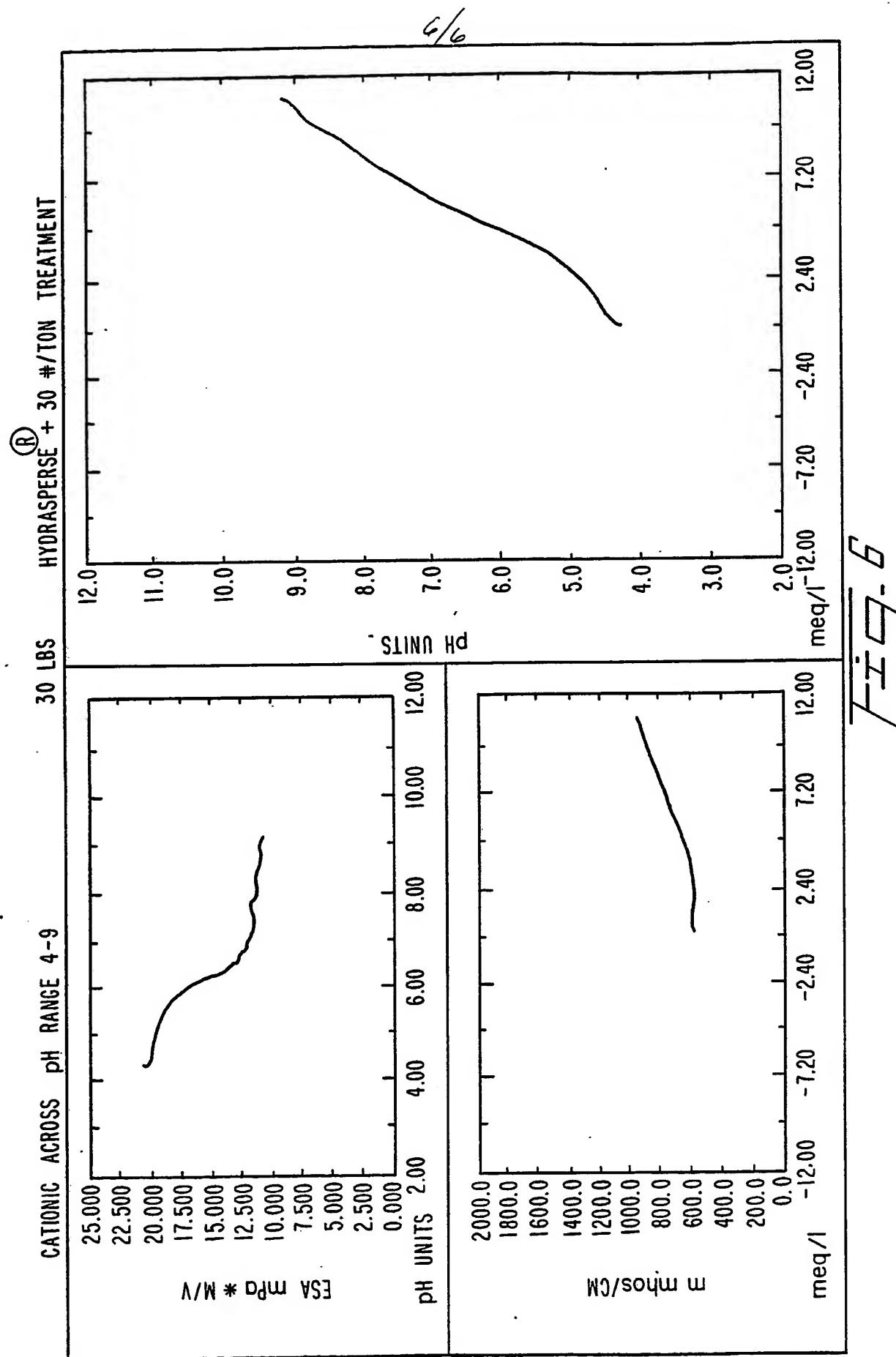
pH UNITS



4/6
7-27-4







INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US88/03635

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (4): C09C 1/42; B01J 20/22; D21F 11/00

U.S. Cl. 106/486; 162/181.6; 501/148, 149

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

| Classification System | Classification Symbols |
|-----------------------|--|
| U.S. | 106/486; 162/181.4, 181.6; 501/145, 146, 147, 148, 149 |

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

| Category ¹⁰ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
|------------------------|--|-------------------------------------|
| X | US, A, 4,030,941 (KUNKLE ET AL) 21 June 1977 See the entire document. | 1, 3, 5, 6, 12-14 |
| Y, E | US, A, 4,788,176 (WIESERMAN ET AL) 29 November 1988 See the entire document. | 2, 4, 17, 18 |
| Y | US, A, 4,445,970 (POST ET AL) 01 May 1984 See the entire document. | 7-10, 15, 16, 19, 20 |

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

03 January 1989

Date of Mailing of this International Search Report

16 FEB 1989

International Searching Authority

ISA/US

Signature of Authorized Officer


THANH DANG